

Beyond Li-Ion – 2012

Beyond Lithium-Ion: A Reality Check

M. Stanley Whittingham,
 Chemistry and Materials Science
 State University of New York
 Binghamton, NY, USA
<http://materials.binghamton.edu>

© M. S. Whittingham 2012

Abstract

➤ Although current Lithium-ion batteries dominate the portable electrochemical storage market, there is limited room for improvement. They have a theoretical energy density approaching **1 kWh/kg**, but in practice deliver no more than 200 Wh/kg. Similarly within a year they will be delivering close to 1 kWh/liter, over 30% of theoretical.

➤ Metal (lithium) oxygen and Lithium sulfur have the capability to exceed these values on a weight basis, and indeed Li/S already does. However, their volumetric capacities are likely to be significantly lower than Li-ion even if all the technical challenges are overcome. I will discuss the opportunities and challenges.

➤ This work is being supported by NYSERDA.

Outline and Challenges

➤ Where have we come from?

➤ Where are we today?

➤ What is the status of intercalation batteries?

➤ What are tomorrow's needs?

- Lower-cost higher energy batteries that are safe
 - Higher volumetric critical for mobile applications
 - Anode limits volumetric energy density
 - Can we use pure metal anodes?

➤ Are conversion reactions the answer?

➤ Can the grand challenge of a "simple" O₂ or S battery be achieved?

- Lithium/air, (or zinc, magnesium or aluminium)
- Can we control air or water?
- Is it worth achieving (aka what is the real storage capacity)?

Redox Intercalation Cathodes for Lithium Ion Batteries

First Generation (1977):
 Layered Sulfides.
 TiS₂ - LiAl - Exxon
 One Lithium to transition metal ratio
 - 480 Wh/kg (240 Ah/kg)

First Commercial Success (1991):
 Layered Oxides.
 LiCoO₂ - LiC₆ - SONY
 0.5 Li to Co cycling - 480 Wh/kg

Today - 2012:
 Mixed layered oxides.
 Li(NiMnCoAl)O₂ – electronics, etc
 LiFePO₄ (& LiMnPO₄?)

EV Show Chicago, 1976

BAE Systems, Binghamton
11 kWh Li-ion
>2000 HEV buses in US

AES, Binghamton
8-20 MW Li-ion

Lithium Dominates the Portable Energy Storage Market
Now Pushing into the Stationary Market

BAE Systems, Binghamton
11 kWh Li-ion
>2000 HEV buses in US

iPad-3

AES, Binghamton
8 MW Li-ion
(flooded)

Intercalation Batteries can be Improved

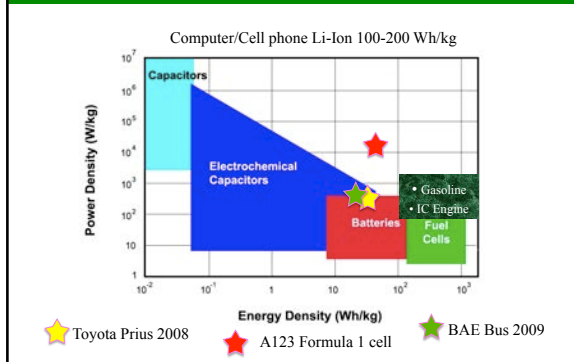
Most of the Energy is Lost in Cell Construction
(Carbon anode major contributor)

Chemistry	Size	Wh/L theoretical	Wh/L actual	%	Wh/kg theoretical	Wh/kg actual	%
LiFePO ₄	54208	1980	292	14.8	587	156	26.6
LiFePO ₄	16650	1980	223	11.3	587	113	19.3
LiMn ₂ O ₄	26700	2060	296	14.4	500	109	21.8
LiCoO ₂	18650	2950	570	19.3	1000	250	25.0
Si-LiMO ₂	18650	2950	919	31.2	1000	252	25.2
Panasonic							

The theoretical values in the table assume only the active components, and no volume or weight for lithium beside that in the cathode.

IEEE Proceedings, Vol. 100, 1518 (2012)

Real Batteries store even less Energy



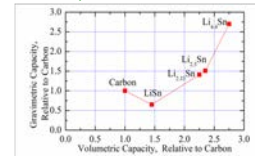
The Anode – Double Capacity to 1.4 Ah/cc

> The Anode

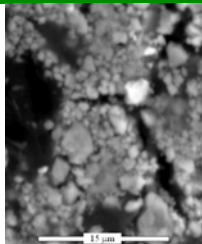
- Make lithium metal work (Holy Grail)
 - + High Energy, > 3000 Ah/kg
 - + High discharge power
 - Electrodeposition
 - Dendrites “always” form
- Protect from air, water, CO₂
 - Use solid electrolyte + pure Li (will need excess)
- Move to tin or silicon
 - + High capacity
 - But high expansion and reactivity



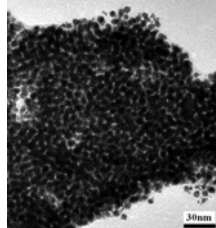
Avestor - AT&T



SONY's Tin Anode is a Smart Nanostructure



SEI layer only formed on surface of microstructure

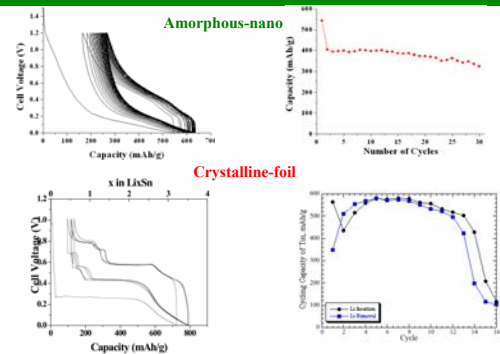


New composite Sn-Co-Ti alloy anodes

23 % tin; 10.3 % cobalt; y % titanium
Sn_{1.1}CoTi_y + carbon

Nano Amorphous Sn-Co has Promising Electrochemistry

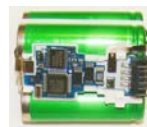
ESL, 10, A274 (2007)



Energy Density of Amorphous Sn-Co still marginal (SONY NP-FP71)

Amorphous-nano

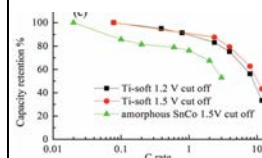
- SONY Nexelion 4 cell Battery
 - 12.2 Wh
 - 128 Wh/kg
 - 256 Wh/L
- Panasonic Si single cell
 - 250 Wh/kg
 - 919 Wh/L



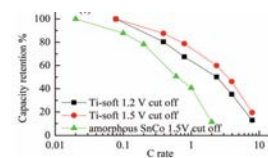
Cobalt gone: nano Sn-Fe-C equally as good (J. Electrochem. Soc., 158, A1498, 2011)

Doubles the Volumetric Capacity of Carbon

Tin-carbon electrode + Fe as Sn₂Fe



Lithium removal – discharge of cell



Lithium insertion – charging of cell

What is the status of Intercalation Batteries

➤ Li-ion intercalation batteries

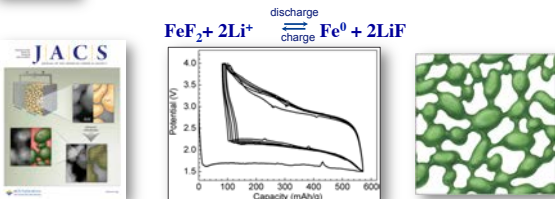
- Approach 800 Wh/kg (excluding C anode)
 - + Lab experimental data
 - + Includes all active components (including oxygen)
 - Cost, beyond raw material, is an issue
 - + Find low cost manufacturing methods
- Volumetric capacity hurt by:
 - Carbon anode
 - Carbon and binder in cathodes
 - Use of nanomaterials
 - Electrodes need to be thicker

What is the status of Conversion Reactions? (Structure destroyed and rebuilt)

➤ NECCES-EFRC studying inorganic materials

- FeF_2 is one example
 - + Large capacity, > 600 Ah/kg
 - Hysteresis, rate and capacity retention are issues
 - Reactivity of nanomaterials a challenge
- Metal- O_2 and metal-S
 - Severe scientific challenges
 - + Large gravimetric capacity, > 800 Ah/kg
 - Protection of anode
 - Hysteresis, rate and capacity retention are issues

Conversion reactions: FeF_2 and CuF_2 (Feng Wang and Jason Graetz, BNL)

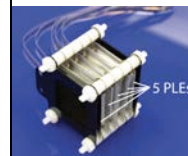


- Goal: Understand reaction mechanisms in conversion electrodes
 - What is the origin of large hysteresis?
 - Why are some systems reversible while others are not?
 - Interconnected Fe 2-3 nm particles allow reversibility
 - Isolated larger Cu particles reduce reversibility

Primary vs Secondary Li/Air-water PolyPlus

Primary Actual Battery Product removed in Sea Water Cell

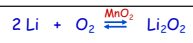
Gravimetric: 1300 Wh/kg
Volumetric: 700 Wh/l



Rechargeable Reality Product Retained in Cell

<http://gigaom.com/>. "Decade-old battery company PolyPlus is the poster child for a high risk, potentially game-changing ARPA-E target. The company is using the ARPA-E grant to build rechargeable lithium-air battery technology that it says can have an energy density of 800 Wh/kg. The secret sauce is in encapsulating the lithium so that it's a stable system. Developing that technology though into commercialization will take years (and already has taken years)."

Can Lithium – Air be made to work? One step and dream toward the Holy Grail

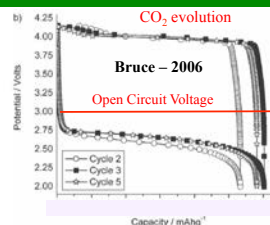


Opportunities:

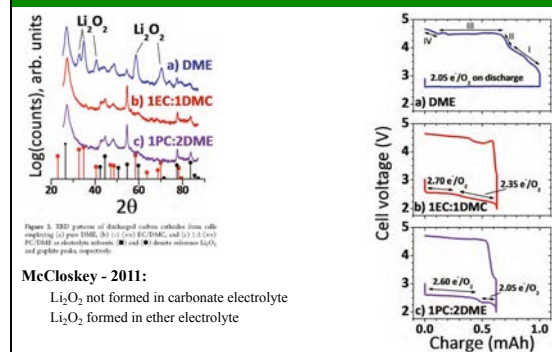
- High capacity
- Low cost, in principle

Challenges:

- Energy Inefficient
- Oxygen Electrocatalyst (both ways)
- Lithium protection
- Lithium electrodeposition (key to all Li batteries)
 - If C_6Li is used energy advantage may be lost
- Containment of electrolyte, if open system
- Containment of Li_2O_2 product in cathode compartment (finite weight)
- What is the reaction mechanism? Is it reversible?
- Elimination of water and CO_2 (may need contained oxygen)



Clue 1. Lithium Peroxide can be formed and partially broken-up on recharge



McCloskey - 2011:

- Li_2O_2 not formed in carbonate electrolyte
- Li_2O_2 formed in ether electrolyte

Clue 2. Oxygen is evolved from Li_2O_2 in ether electrolyte (McCloskey et al, JPCL 2_1161_2011)

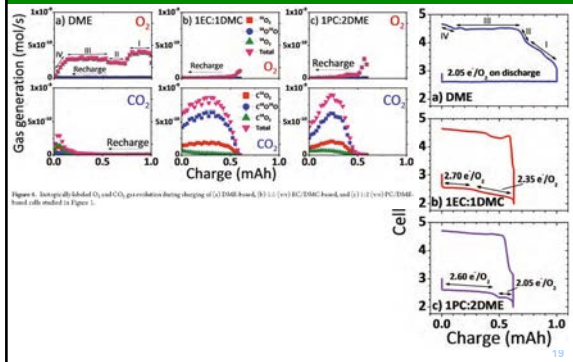


Figure 4. Gas generation (mol/s) and CO_2 evolution during charging of (a) DME, (b) 1EC:1DMC, and (c) 1PC:2DME. Based on data in Figure 3.

What is the reaction mechanism of Li-Air?

> Aqueous system

- LiOH
- Soluble, maybe more easily recharged

> Non-aqueous system

- $\text{O}_2 + \text{Li}$ gives LiO_2 , then what?
- Ideally Li_2O_2 then Li_2O
- In reality, LiO_2 reacts with carbonate solvents, but
 - Ethers show some stability
 - Reaction is reversible, $^{18}\text{O}_2$ in and out at low potentials
 - At higher potentials CO_2 evolved from solvent
 - Suggests that electrocatalyst may not be desirable/effective
 - McCloskey, JACS 2011
- Theory (Ceder) suggests that charging overpotential is function of Li_2O_2 crystal face (Phys Rev 2011)

What is the real storage capacity of Li-Air? (Based on Li_2O_2)

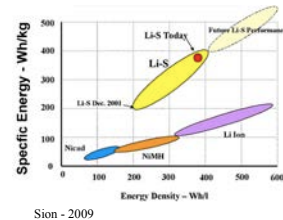
- > Lab Energy density may be double that of Li-ion if all works out well
- > Lab Volumetric energy density same as Li-ion
 - > Likely to be much lower, pumps/air ingress etc

System	Energy Density Wh/kg	Energy Density Wh/L	Assumptions Made
C-Lithium-ion	416	1450	3.7 volts, 180 Ah/kg actual cathode
C-Lithium-air	706	1600	2.5 volts, no weight added for catalyst or carbon
Lithium-LiMO ₂	971	2000	4 volts, 278 Ah/kg cathode, 3 x Li
Lithium-air	2050	2090	2.8 volts, 3xLi, no catalyst, carbon or solid electrolyte

IEEE Proceedings, Vol. 100, 1518 (2012)

What is the real storage capacity of Li-O₂ vs Li-S?

- > Lab Li-O₂ Energy density may be double that of Li-ion if all works out well
 - Li-S much higher than Li-ion, possibly higher than Li-air
- > Lab Li-O₂ Volumetric energy density will be less than Li-ion
 - Li-S less than Li-ion



Sion - 2009

Other Metal-Oxygen Cells may be attractive

Metal/Oxygen Energy Densities (ED)

MeO	ΔG kJ/O ₂	V, Volts	ED Wh/kg	ED Wh/L
CaO	1200	3.11	2972	9960
MgO	1170	3.03	4032	14400
Li_2O_2	1150	2.98	3487	8050
Li_2O	1130	2.93	5252	10600
Al_2O_3	1060	2.75	4332	17300
Na_2O	760	1.97	1703	3870
ZnO	650	1.68	1109	6220

Conclusions – Li-Air/S Batteries

- > Need fundamental research on reaction mechanisms
 - Non-aqueous more difficult, need some solubility of Li_2O_2
 - Aqueous may be easier
- > Need fundamental research on the lithium anode – helps all Li batteries
 - Electrodeposition – no dendrites
 - Reduce amount of excess lithium needed from 3x
- > Need an impervious stable (dual) electrolyte
 - Ceramic or polymer

